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Polymer Equations of State and Shock-Driven Decomposition

Josh Coe

Physics & Chemistry of Materials (T-1)
Los Alamos National Laboratory

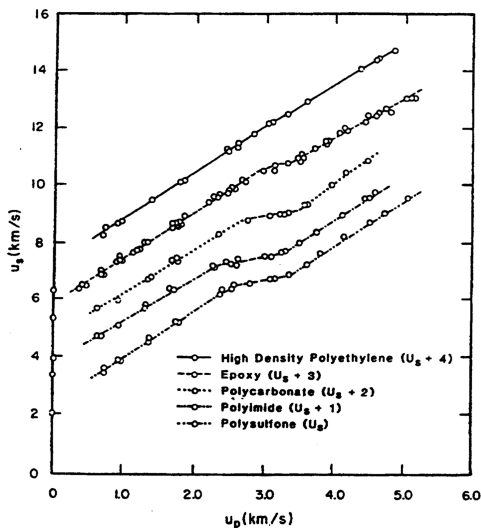
October 28, 2019



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Polymer Hugoniots Display Structure

- Derivative discontinuities at $u_p \sim 3$ km/s (typically $P \sim 25$ GPa)
 - Middle line segment not at equilibrium

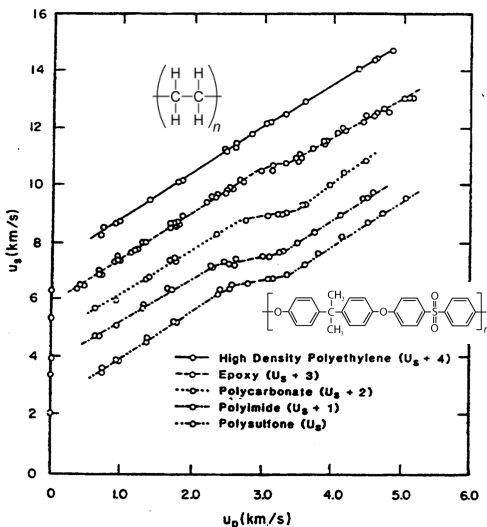


LA-13006-MS, LANL (originally prepared in 1977)

Polymer Hugoniots Display Structure

- Derivative discontinuities at $u_p \sim 3$ km/s (typically $P \sim 25$ GPa)
 - Middle line segment not at equilibrium
- Volume collapse in P - V
 - Degree of collapse correlates qualitatively with chemical structure

Material name	$P_{\text{threshold}}$ (GPa)	$\Delta V_{\text{tr}}/V(\%)$
epoxy	23.1	3.9
PMMA	26.2	3.4
PTFE	41.6	1.1
PE (linear)	24.7	0.4
polycarbonate	20.0	11.4
phenolic	23.2	6.7
polysulfone	18.5	12.9
polyurethane	21.7	7.3



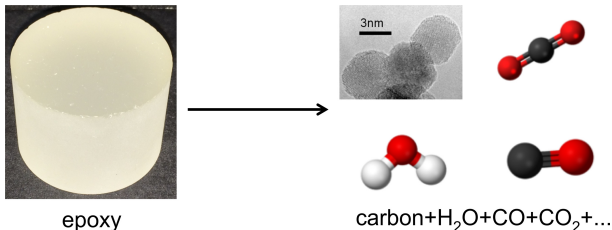
LA-13006-MS, LANL (originally prepared in 1977)

Hugoniot Structure: Two Early Views

- Phase transition (LANL, 1977)
 - analogous to graphite→diamond
 - “compression...is two-dimensional in nature” below the transition, “more typical of a three-dimensional solid” above

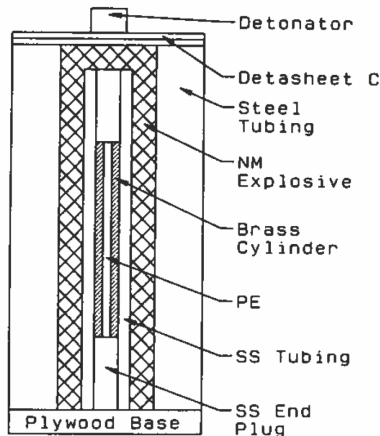
Hugoniot Structure: Two Early Views

- Phase transition (LANL, 1977)
 - analogous to graphite→diamond
 - “compression...is two-dimensional in nature” below the transition, “more typical of a three-dimensional solid” above
- Decomposition (LLNL, 1979)
 - “..hydrocarbons at high pressure ($\gtrsim 10$ GPa) and high temperature ($\gtrsim 1000$ K) dissociate into carbon in the diamond phase and hydrogen in a condensed molecular phase”



Hugoniot Structure: Recovery Experiments

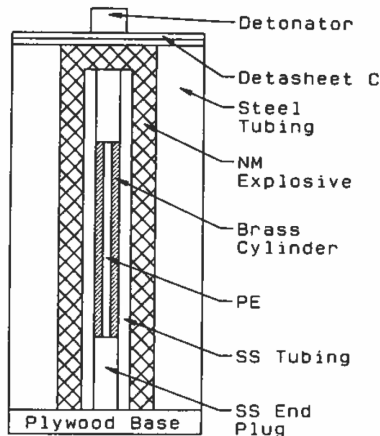
- Experiments on polyethylene and Teflon
- Setup
 - Single-shock, Mach compression
 - Hermetically-sealed capsule
 - Enabled recovery of soot and gases
 - Mass spectrometry, XRD, TEM



PE: SCCM-1989, p. 687; PTFE: *J. Chem. Phys.* **80**, 5203 (1984)

Hugoniot Structure: Recovery Experiments

- Experiments on polyethylene and Teflon
- Setup
 - Single-shock, Mach compression
 - Hermetically-sealed capsule
 - Enabled recovery of soot and gases
 - Mass spectrometry, XRD, TEM
- Polyethylene results
 - Polymer recovered at ~ 20 GPa
 - Gases and soot recovered 28-40 GPa
 - Gases were $>80\%$ mol CH_4 and H_2
 - Soot was neither graphite nor diamond



PE: SCCM-1989, p. 687; PTFE: *J. Chem. Phys.* **80**, 5203 (1984)

Unreactive EOS: SESAME Framework

- Purely volumetric, no strength or viscoelasticity
- 3-part decomposition for free energy of each phase

$$F(\rho, T) = \phi(\rho) + F_{\text{ion}}(\rho, T) + F_{\text{elec}}(\rho, T)$$

- Minimize F as function of mass fractions \rightarrow equilibrium phase boundaries

Unreactive EOS: SESAME Framework

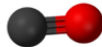
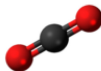
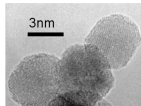
- Purely volumetric, no strength or viscoelasticity
- 3-part decomposition for free energy of each phase

$$F(\rho, T) = \phi(\rho) + F_{\text{ion}}(\rho, T) + F_{\text{elec}}(\rho, T)$$

- Minimize F as function of mass fractions \rightarrow equilibrium phase boundaries
- With regard to polymers:
 - Electronic part not that important for $\rho/\rho_0 \lesssim 3$
 - Ionic models are variations on Debye
 - Cold curve extracted from fit to shock data
 - This produces artifacts if data above cusp included

Thermochemical Modeling

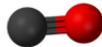
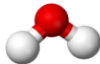
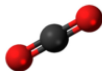
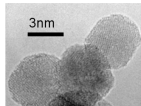
- Decomposition products as mixture of fluids and bulk solids
 - Each constituent has its own free energy model
 - Fluids: spherical, pairwise interaction potential translated to free energy with perturbation theory
 - Solids: SESAME model
 - Mixture rule required (non-unique)



carbon+H₂O+CO+CO₂+...

Thermochemical Modeling

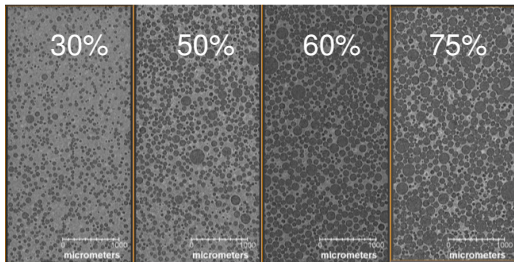
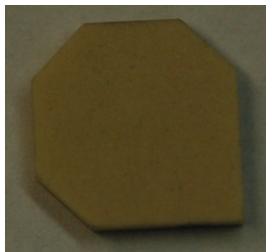
- Decomposition products as mixture of fluids and bulk solids
 - Each constituent has its own free energy model
 - Fluids: spherical, pairwise interaction potential translated to free energy with perturbation theory
 - Solids: SESAME model
 - Mixture rule required (non-unique)
- Assume full thermodynamic (and thus, chemical) equilibrium
 - Adjust concentrations until minimal free energy found and stoichiometry preserved
- Reaction energy (E_0) tuned to fit shock data



carbon+H₂O+CO+CO₂+...

See talks by Leiding, Ticknor

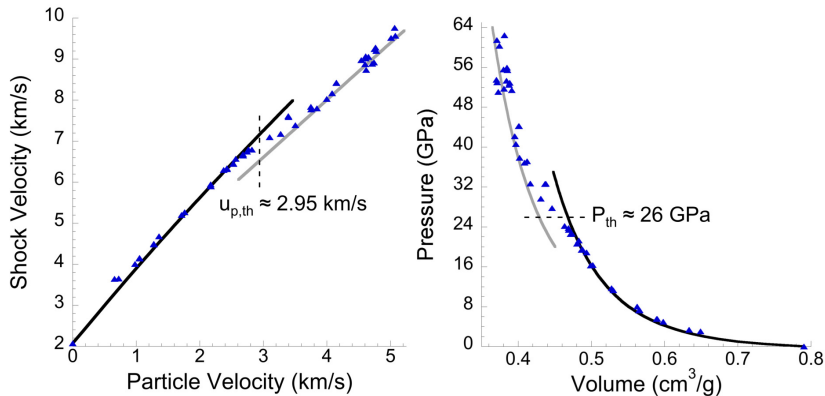
PMDI Polyurethane: Approach



- Shock data for polyurethane at 0-75% porosity
- Thermochemical modeling above some threshold
 - Threshold varies with porosity, unknown a priori
 - Carbon as diamond for full density, as graphite for foams
 - Only adjustable parameter is E_0
- Reactants were SESAME + $P - \alpha$ porosity model
 - Only porous parameter is crush pressure, P_c

Dattelbaum & Coe, et al., *J. Appl. Phys.* **115**, 174908 (2014)

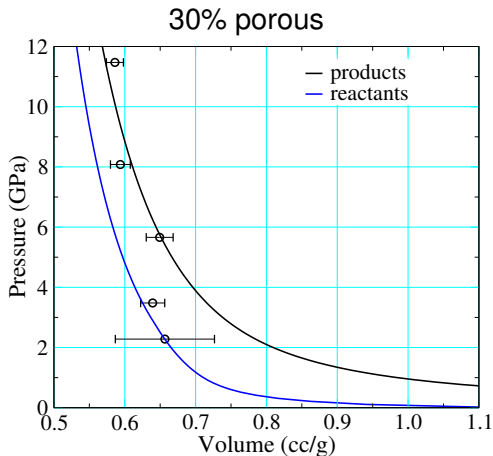
PMDI Polyurethane: Full Density Results



- E_0 of products adjusted to match data above transition
- Reactant EOS calibrated to all solid data

Dattelbaum & Coe, et al., *J. Appl. Phys.* **115**, 174908 (2014)

PMDI Polyurethane: Foamed Results

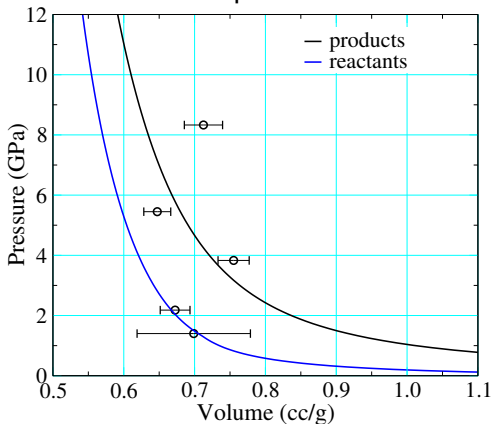


- Porous E_0 same as for solid
 - Good agreement with highest points
- Set $P_c=16$ kbar
- Products locus to right of reactants

Dattelbaum & Coe, et al., *J. Chem. Phys.* **115**, 174908 (2014)

PMDI Polyurethane: Foamed Results

50% porous

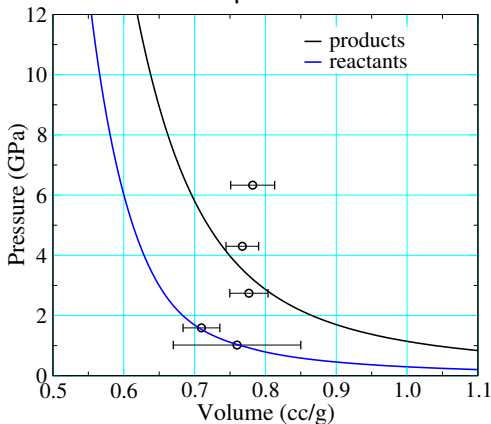


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PMDI Polyurethane: Foamed Results

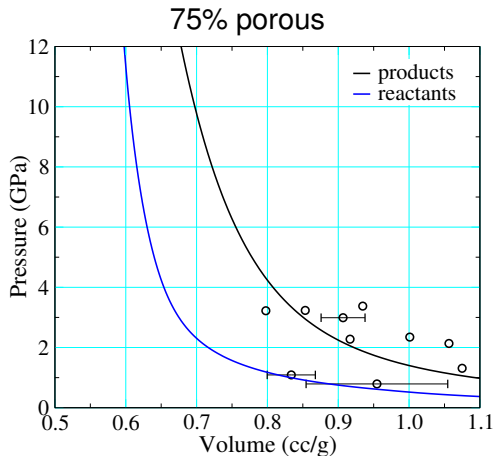
60% porous



- Porous E_0 same as for solid
 - Good agreement with highest points
- Set $P_c=16$ kbar
- Products locus to right of reactants

Dattelbaum & Coe, et al., *J. Chem. Phys.* **115**, 174908 (2014)

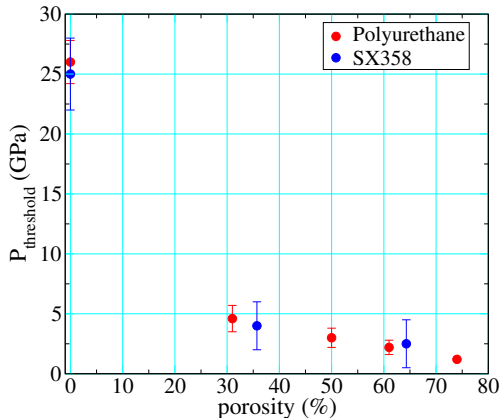
PMDI Polyurethane: Foamed Results



- Porous E_0 same as for solid
 - Good agreement with highest points
- Set $P_c=16$ kbar
- Products locus to right of reactants
- Approach makes qualitative sense of the pattern
- Uncertainties are an issue

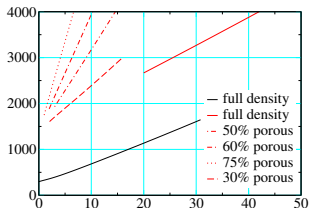
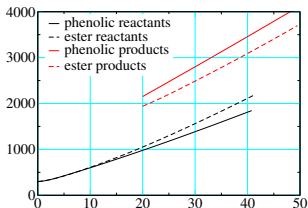
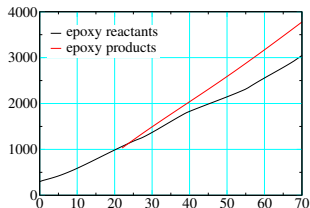
Dattelbaum & Coe, et al., *J. Chem. Phys.* **115**, 174908 (2014)

Transition “Thresholds”



- Roughly exponential drop
- Strong dependence on timescale of experiment

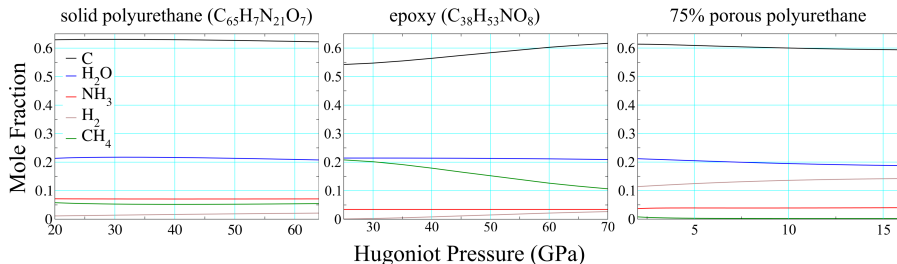
Temperature Usually Increases



- In most cases we find $T > 0$ upon decomposition
- Foam temperatures very high due to $P - V$ work
- High T observable in “bleached” PDV signal

Dattelbaum and Coe, *Polymers* (2019)

Product Compositions



- Products dominated by solid carbon and water
- Not much variation over range of gun data or with porosity
- Hard to validate these (see Leiding and Lindsey talks, Jadrich poster)

Dattelbaum and Coe, *Polymers* (2019)

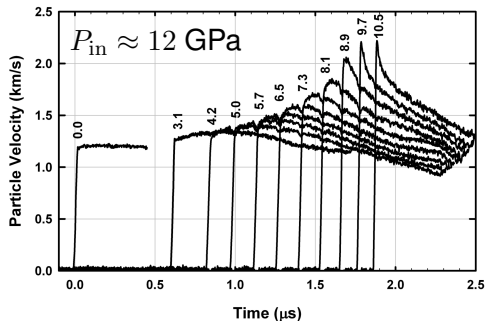
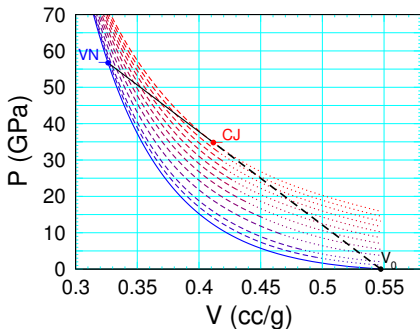
The Hydrodynamic Connection

- “Chemistry” to the Euler equations:

ΔE and ΔV , smeared out over some Δt

- ΔE can be incorporated through EOS or source term
 - ΔV always incorporated through EOS
- The signs of the Δ 's determine the character of the waveforms
 - The sign of ΔV is important
- Simulating reactive wave profiles involves 3 ingredients:
 - EOS
 - rate model/closure rule
 - integration of the conservation equations

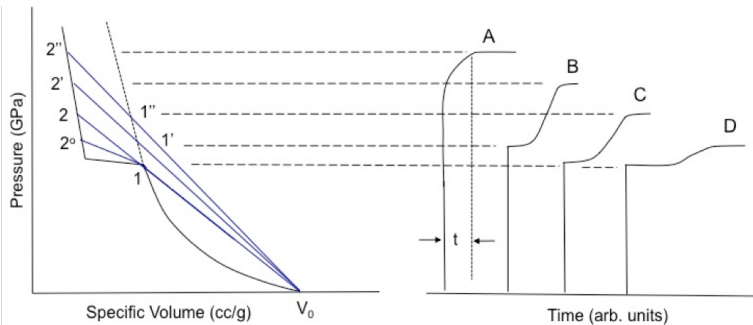
Reactive Wave Profiles: Energetic Materials



- ZND: inert shock followed by reaction zone to CJ state
- Reaction behind feeds the front, strengthening lead shock
- Reaction pushes unsteady \rightarrow steady

Menikoff, LA-UR-15-29498; Gustavsen, et al., *J. Appl. Phys.* 2006

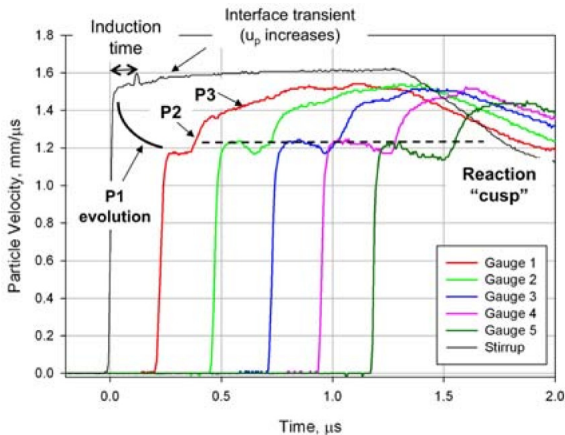
Reactive Wave Profiles: Non-Energetic



- Reaction behind weakens lead shock
- Waves separate rather than converge
- Initial (P1) wave decays, second (P2) wave carries to products
- Decay and rise times contain kinetic information

Dremin, Combust. Explos. Shock Waves (1965); Dattelbaum AIP Conf. Proc. (2018)

Reactive Wave Profiles: Organic Liquids

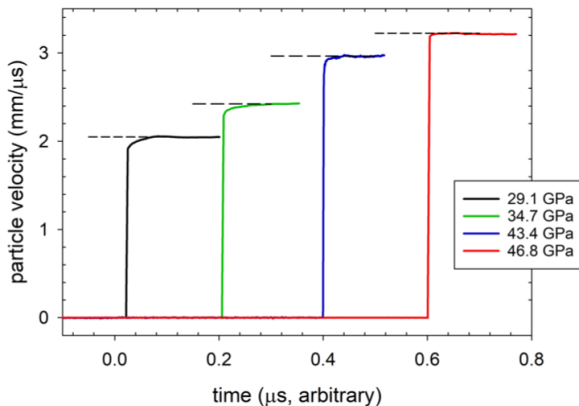


Embedded gauge data for liquid phenylacetylene

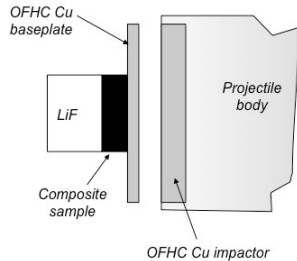
Dattelbaum & Sheffield, *AIP Conf. Proc.* **1426**, 627 (2012)

Reactive Wave Profiles: Polymers

Transmission data for fiber-filled composites



VISAR at (reshock) interface with window

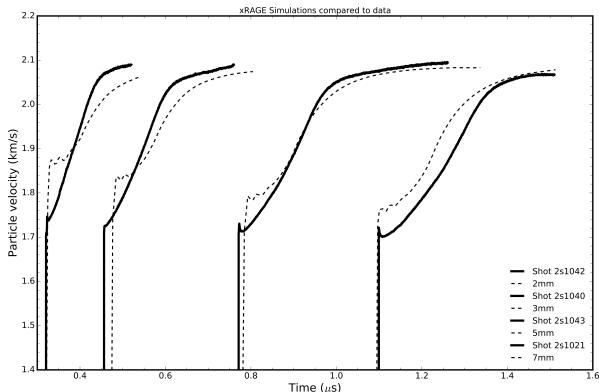


- First observation of multiwave structure in reacting polymer

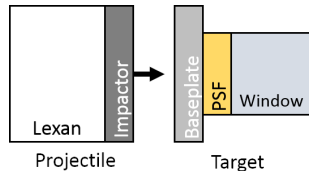
Dattelbaum & Coe, et al., *J. Appl. Phys.* **116**, 194308 (2014)

Reactive Wave Profiles: Polymers

increasing sample thickness \rightarrow



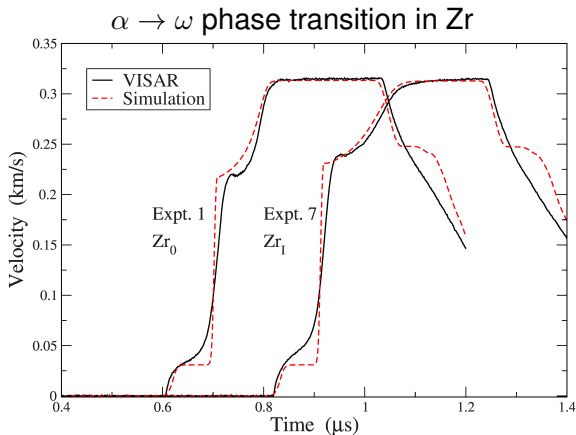
PDV at (reshock)
interface with window



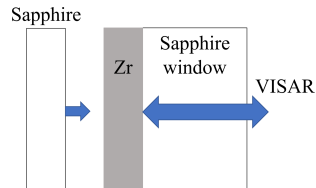
- Increased P1-P2 lag \Rightarrow wave separation with time
- Dotted lines are simulation with Arrhenius model

R. Huber, et al., submitted to J. Appl. Phys.

“Reactive” Wave Profiles: Metals



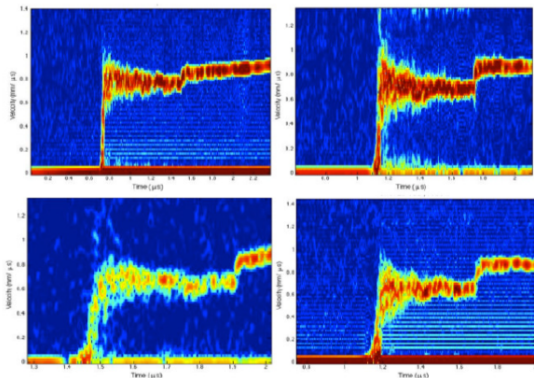
VISAR at (reshock)
interface with window



Rigg, et al., *J. Appl. Phys.* (2009)

Reactive Wave Profiles: Foams

PDV in polyurethane foams



- Clockwise from upper left: 30%, 50%, 60%, 75% porous
- One wave observed
- PDV increasingly “washed out” due to high T

Dattelbaum & Coe, et al., *J. Appl. Phys.* **115**, 174908 (2014)

Summary

- Polymers decompose under shock loading
 - $u_p \sim 3$ km/s, $P \sim 25$ GPa at full density
- Threshold conditions drop dramatically as porosity increases
 - Products expand upon reaction
- Wave splitting a feature of density-increasing transitions
 - Chemically more like HE, but wave profiles more like phase transitions in metals, etc.
- Papers
 - In progress: polysulfone, PMMA, polyimide
 - Previous: polyethylene (JAP, 2019), overview (Polymers, 2019), polyurethane (JAP, 2014), fiber-filled composites (JAP, 2014), lots of conference proceedings

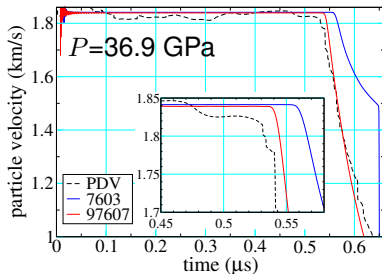
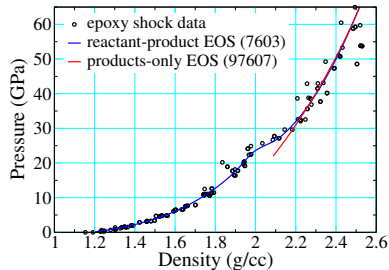
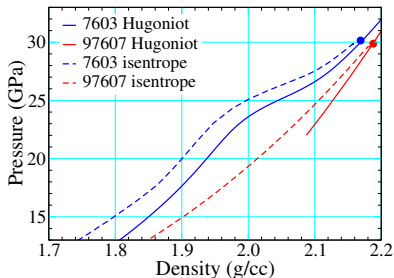
Acknowledgements

- (LANL Fellow) Dana D
- experiments: Rachel Huber, John Lang, Rick Gustavsen
- simulations: Jeff Peterson, Katie Maerzke
- OpenSesame: Tinka Gammel
- Magpie: Charles Kiyanda, Jeff Leiding, Chris Ticknor, Stephen Andrews
- \$: Science Campaign 2, ASC PEM

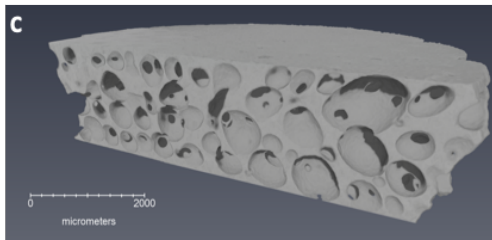
Extra Slides

Artificial Multiwave Structure

- Products EOS 97607
- Historical EOS 7603
 - structure included in fit
 - produces multiwave structure
 - structure preserved in isentropes
- Reversibility?



Heterogeneous Materials are Hard



- Not always clear what you're probing
 - Pore diameters span range $\mathcal{O}(10\ \mu\text{m} - 1\ \text{mm})$
 - Spot size of our standard PDV is roughly $450\ \mu\text{m}$
- $U_S \approx u_p$, so $\sigma(\rho)$ large
- Shot-to-shot variability > known sources of uncertainty
- We have the same problem with powders

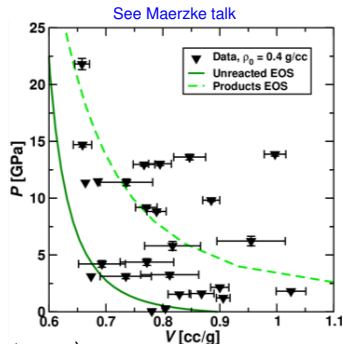


Image courtesy of Brian Patterson (MST-7, LANL), data courtesy of John Lang (M-9, LANL)

Detonation Criterion

- In order to produce a self-sustaining wave, a material must have a positive thermicity coefficient, σ :

$$\sigma = \left(\frac{\partial P}{\partial \lambda} \right)_{V,E} = \frac{\Delta V}{V} - \frac{\Gamma}{c^2} \Delta H$$

λ = reaction progress variable

Γ = Grüneisen parameter

c = frozen sound speed

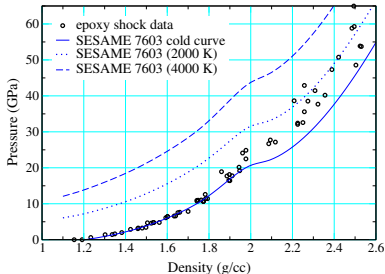
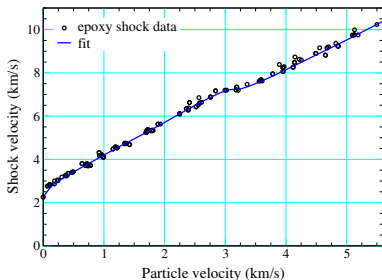
ΔH = enthalpy change

- Exothermicity ($\Delta H < 0$) isn't sufficient (or even necessary!) for detonation
 - "The importance of the volume term has often been overlooked..."

Fickett and Davis, *Detonation: Theory and Experiment*

Our Traditional Approach to Polymer EOS

- Fit some shock data
- Assume some characteristic temperature
 - Cold curve by subtraction
- Potential problems:
 - Structure present even at 0K
 - Structure preserved to high T
 - Completely reversible transition
- Thermals often poorly constrained
 - Important for foams



Rate Model Calibration: Theory

- Adiabatic induction time for constant-volume burn

$$t_{\text{ad}}(T_0) = \frac{T_0^2}{\nu T_a (T_1 - T_0)} e^{(T_a/T_0)}$$

T_0 = reactant temperature

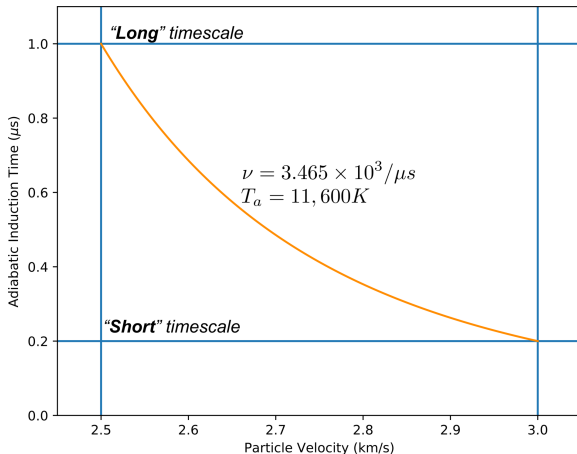
T_1 = product temperature

ν = frequency factor (parameter)

T_a = activation temperature (parameter)

- In our case, these are Hugoniot temperatures
- There's a problem when reaction lowers temperature
- Because $T_0 = T_0(u_p)$, we'll consider $t_{\text{ad}}(u_p)$

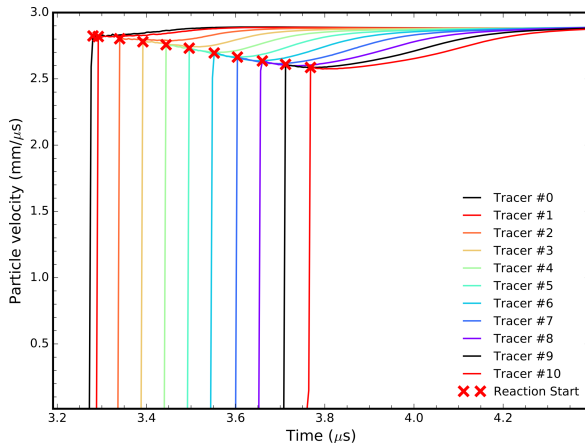
Rate Model Calibration: Practice



- Using $1/(\text{adiabatic induction time})$ as proxy for rate
- For a given pair of EOS:
 - T_a sets u_p range
 - ν shifts laterally

Simulated Wave Profiles in Polysulfone

- $P_{\text{input}}=22.1$ GPa; transition starts ~ 18.5 GPa



- Qualitative features good, but experimental reaction signatures (P1 decay, P2 rise) much more subtle